UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 46: THE ACTION OF LIQUEFIED AMMONIA ON CHROMIC CHLORIDE, BY W. R. LANG AND C. M. CARSON

NOTE ON THE ACTION OF METHYLAMINE ON CHROMIC CHLORIDE, BY W. R. LANG AND E. H. JOLLIFFE

(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. XXVI.)

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[Reprinted from The Journal of The American Chemical Society,
Vol. XXVI. No. 4. April, 1904.

THE ACTION OF LIQUEFIED AMMONIA ON CHROMIC CHLORIDE.

By W. R. Lang and C. M. Carson.

Received January 30, 1904.

Jörgensen describes a number of compounds derived from chromic chloride by the action on chromous chloride of aqueous ammonia, ammonium chloride and subsequent oxidation.

The authors have obtained similar substances by the direct action of dry liquid ammonia on violet chromic chloride at low temperatures. Violet chromic chloride is not acted upon by aqueous ammonia nor by dry ammonia gas, but liquid ammonia acts upon it readily, completely transforming it into a salmon-colored powder.

Experimental.—Three grams of powdered chromic chloride were placed in a vessel made of combustion tubing, closed at the lower end and drawn out at the neck to allow of the tube being sealed at the blowpipe. The whole was placed in a freezing-mixture, consisting of solid carbonic acid and ether, and ammonia, dried over potassium hydroxide, was passed in. No action took place until liquefaction began, when the chromic chloride swelled up and became pasty, the color changing at the same time to a dark salmon-pink. Ammonia in considerable excess was allowed to accumulate on the top of the mass and the tube was then sealed. The tube containing the salmon-colored material was set aside for a week at the room temperature, being shaken occasionallly to insure thorough mixing. Subsequent experiments showed the action of the ammonia to have been complete from the first, so in preparing further quantities this was omitted. The liquid ammonia on standing separated out colorless. The tube was then cooled to —35° and opened, the temperature raised gradually to 0°, at which it was kept constant for twenty-four hours, and the dry powder remaining kept for investigation. Further quantities were prepared in the same way and left standing at 0° for two and four days respectively. Another portion of the powder was left at 15° C. for two days, and yet another portion was heated to 110° C. for the same length of time when the color became more distinctly pink. Analyses of the powder obtained at 0°, 15°, and 110° respectively yielded:

	(A) At 0°. Per cent.	(B) At 15°. Per cent.	(C)[1] At 110°. Per cent.
Chromium	20.1	20.6	21.7
Chlorine	41.1	41.6	44.1
Ammonia	38.6	37.8	34.1
	99.8	100.0	99.9
Corresponding to molecules of NH_3 per molecule of Cr_2Cl_6	11.7	11.2	9.7

[1] This analysis was done by Mr. J. A. M. Dawson.

Further heating continued for twenty-four hours to 130° brought about the separation of a small amount of chromic oxide but complete decomposition into chromic oxide did not take place until a temperature of 180° was reached.

From the analytical results it was evident that the powders contained a mixture of substances, and the following investigation led to the isolation of two definite compounds therefrom.

I. The powder which had remained at 0° was treated with a small quantity of cold water, 5 cc. to every gram of the substance. Partial solution took place, and on filtering off from the undissolved solid, a clear solution of a brown color was obtained, which on standing in the air for even a short time, evolved ammonia and deposited chromium hydroxide. On removing the precipitated chromium hydroxide and rapidly evaporating *in vacuo*, yellow crystals separated out, which were collected and dried between filter-paper (for convenience let α indicate the yellow crystals). The residue from this first extraction with water was treated in the cold with a further quantity of the solvent and filtered. Evaporation *in vacuo* yielded, when carefully conducted, red crystals (β). When the concentration in the vacuum desiccator was conducted too slowly, slight decomposition into gelatinous chromium hydroxide took place with the evolution of ammonia, but if rapidly conducted in shallow evaporating dishes, the crystals separated readily from the solution and no ammonia was evolved. Analysis of the yellow compound and the red compound gave:

	α-Salt. Per cent.	β-Salt. Per cent.
Chromium	18.7	21.52
Chlorine	38.0	43.20
Ammonia	36.6	35.00
Water (by difference)	6.7	0.00
	100.00	99.72

The composition of the yellow α-compound thus corresponds with the formula $Cr_2Cl_6,12NH_3,2H_2O$, and that of the red β-compound with $Cr_2Cl_6,10NH_3$.

II. The powder obtained by keeping the original substance at 15° was similarly extracted with water, and from it were obtained yellow and red crystals, whose composition and properties were identical with the α- and β-compounds obtained in I.

III. Treatment of the original pink substance with cold water,

which had been maintained for two days at 100° C., yielded no α-crystals, but the red β-compound only.

PROPERTIES OF THE α-AND β-CRYSTALS

The yellow crystals are soluble in water, but insoluble in hydrochloric acid and in alcohol. From the aqueous solution all the chlorine is precipitated in the cold by silver nitrate. On standing at 110° for two days, the yellow crystals are changed partly into a red powder, with separation of chromic oxide. These crystals evidently correspond with the *luteochromium* compounds obtained by Jörgensen[1] of the general formula $Cr_2 12NH_3X_6$.

The red compound crystallizes in small perfectly formed cubes and octahedra. They dissolve in cold water slowly while hot water causes a separation of chromium hydroxide. Hydrochloric acid and alcohol exert no solvent action on them. Further, when the crystals are treated with liquid ammonia, no change takes place, and on addition of a small quantity of violet chromium chloride to the mixture of the salt and ammonia the chromic chloride reacts at once with the ammonia, yielding a pink powder from which the β-crystals may be separated mechanically. On treating the mixed crystals and powder with cold water, the latter readily dissolved away, leaving the red crystals untouched. The composition of this β-compound, $Cr_2 10NH_3Cl_8$, points to its being *chlorpurpureochromium chloride.*

CHEMICAL LABORATORY, UNIVERSITY OF TORONTO.

NOTE ON THE ACTION OF METHYLAMINE ON CHROMIC CHLORIDE.

BY W. R. LANG AND E. H. JOLLIFFE.

Received January 30, 1904.

A SOLUTION of methylamine was gently heated and the gas conducted through drying towers filled with potassium hydroxide to a glass tube containing chromium chloride and immersed in a freezing-mixture at a temperature of —10°. As soon as the liquid methylamine collected in the tube, combination between it and the chromic chloride took place and a substance of a pale pink color, closely resembling the ammonia compound (Lang and Carson), was formed. The excess of methylamine was allowed to pass off

[1] *J. prakt. Chem.*, [2] 30, 1.

and the contents of the tube dissolved in water. The substance was very soluble and the least possible quantity of water was used. The solution, on rapid evaporation *in vacuo*, yielded dark red crystals. Considerable difficulty was experienced in obtaining these crystals, owing to the rapidity with which the solution decomposed into chromic hydroxide; consequently the analysis of the crystals obtained by repeated operations had to be made on very small quantities. Analysis of the crystals thus obtained from the compound at a temperature of 15° gave:

	Found. Per cent.	Calculated for $Cr_2Cl_6 10CH_3NH_2$. Per cent.
Chromium	16.25	16.68
Chlorine	35.20	33.92
Methylamine	48.50	49.6
	99.95	100.00

Crystals produced in a similar manner from the original compound, previously heated to 94°, gave:

	Found. Per cent.	Calculated. Per cent.
Chromium	16.55	16.61
Chlorine	34.19	33.86
Methylamine	48.89	49.53
	99.63	100.00

The composition of these crystals is therefore $Cr_2Cl_6, 10CH_3NH_2$, corresponding to the similarly constituted chloropurpureochromium chloride obtained (Lang and Carson) from anhydrous ammonia and chromic chloride.

On heating to 100° the compound formed by the direct action of methylamine on chromic chloride, analysis showed it to contain 43.26 per cent. of methylamine, which would point to its composition being $Cr_2Cl_6, 8CH_3NH_2$, the percentage in this latter being 43.8. At 124° C. complete decomposition into Cr_2O_3 took place.

The analogy between the crystals thus obtained and the chloropurpureo compound is evident. The great difficulty of obtaining pure methylamine on the American continent prevented the investigation of these substances being continued further or more accurate analyses being made. Aniline and methylaniline had no action on the violet chromic chloride whether in the cold or when heated together. The effect of heating for any length of time in a sealed tube was not tried.

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